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The principal objective of this course of study was the development of detailed kinetic mechanisms which described the oxidation of simple compounds in supercritical water at the elementary reaction level. The compounds chosen were hydrogen and carbon monoxide. Kinetic mechanisms were developed from corresponding high-temperature, low-pressure combustion mechanisms available in the literature. The mechanisms were adapted to the high-pressure conditions of the SCWO environment and the resulting modified mechanisms were used to predict the temporal behavior and temperature and pressure dependence of the oxidation of each compound. The model predictions were then compared to hydrogen and carbon monoxide oxidation data obtained from experimental work carried out in parallel to the kinetic modeling effort.

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**DESTRUCTION OF HAZARDOUS CHEMICALS BY
OXIDATION IN SUPERCRITICAL WATER:**

**A THEORETICAL AND COMPUTATIONAL TREATMENT OF
MECHANISMS AND ELEMENTARY REACTIONS**

FINAL REPORT

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1.0 STATEMENT OF PROBLEM STUDIED

The principal objective of this course of study was the development of detailed kinetic mechanisms which described the oxidation of simple compounds in supercritical water at the elementary reaction level. The compounds chosen were hydrogen and carbon monoxide. Kinetic mechanisms were developed from corresponding high-temperature, low-pressure combustion mechanisms available in the literature. The mechanisms were adapted to the high-pressure conditions of the SCWO environment and the resulting modified mechanisms were used to predict the temporal behavior and temperature and pressure dependence of the oxidation of each compound. The model predictions were then compared to hydrogen and carbon monoxide oxidation data obtained from experimental work carried out in parallel to the kinetic modeling effort.

2.0 SUMMARY OF RESULTS AND KEY FINDINGS

2.1 HYDROGEN OXIDATION IN SUPERCRITICAL WATER

2.1.1 Experimental results

A total of fifty-five hydrogen oxidation experiments were conducted in sub- and supercritical water in an isothermal, isobaric, tubular flow reactor. Experimental operating temperatures and pressures were varied over a range of 495-600°C and 118-246 bar. Reactor residence times ranged from 3.4 to 11.0 seconds. Inlet oxygen-to-hydrogen molar ratios were varied between 0.125 and 11.82--both above and below the stoichiometric value of 0.5. The inlet hydrogen and oxygen concentrations for all experiments were dilute--varying from 0.4×10^{-6} to 4.5×10^{-6} mol/cm³. Observed conversions ranged from 6.1 to 98.2%. A more detailed discussion of experimental conditions and methodologies and a description of the experimental apparatus can be found in the publications by Holgate (1993), and Holgate and Tester (1993, 1994a)

Hydrogen oxidation under the conditions described above was found to possess a pronounced induction time on the order of 1-2 seconds. The induction time and the subsequent consumption of hydrogen were found to be weakly dependent on concentration for a stoichiometric hydrogen-oxygen mixture at 550°C over a three-fold variation in hydrogen inlet concentration. In addition, the oxidation of hydrogen was found to be strongly pressure dependent over the experimentally-accessible operating range, with higher pressures favoring higher rates of oxidation. The apparent, first-order rate constant regressed from a set of isothermal data was found to increase approximately an order of magnitude over an operating pressure range of 118 to 246 bar. A complete description and discussion of the experimental results can be found in Holgate (1993) and in Holgate and Tester (1993, 1994a), and Holgate et al (1993).

2.1.2 Elementary reaction modeling

An elementary reaction model for hydrogen oxidation in supercritical water was constructed and was found to be quite successful in reproducing the experimentally observed temporal behavior and pressure dependence of the data. The model, however, slightly under predicts both the length of the induction time and the rate of hydrogen conversion. The model was comprised of 19 reversible, elementary reactions involving 4 stable species (H_2 , O_2 , H_2O , H_2O_2) and 4 radical intermediates (HO_2 , OH , H , and O).

Analysis of the mechanism suggests that the oxidation of hydrogen occurs primarily via the reaction $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$. Since this step is first-order in hydrogen, so too is the overall oxidation process (a mechanistic conclusion in agreement with the data). The model also suggests that oxygen participates in the mechanism through the rapid conversion of H to HO_2 ; since this step is fast, the overall oxidation does not depend on the oxygen concentration (also in agreement with the experimental data). Once formed, HO_2 disproportionates to H_2O_2 and OH . H_2O_2 generated then dissociates to form two more OH radicals. The three OH radicals can then participate in the primary oxidation step.

A combined sensitivity and reaction path analysis of the mechanism reveals that the pronounced experimentally-observed pressure effect can be largely accounted for by the role of water as a reactive species in the highly-sensitive branching reaction, $\text{H}_2\text{O} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{OH}$. This reaction is greatly accelerated--relative to typical gas-phase oxidation conditions--by the high water concentrations (densities) present in supercritical water. Increasing operating pressures result in higher water concentrations, which, in turn, accelerate the rate at which H_2O_2 and OH are generated. Thus, the majority of the pressure dependence of the oxidation rate can be ascribed to the effect of changing water concentration (density) on the rate of the branching reaction. A detailed analysis and discussion of the hydrogen oxidation mechanism and its development is presented in Holgate and Tester (1993, 1994b).

2.2 CARBON MONOXIDE OXIDATION IN SUPERCRITICAL WATER

2.2.1 Experimental results

The oxidation of carbon monoxide in supercritical water was investigated in forty-three experiments over a temperature range of 420-571°C and a pressure range of 118-246 bar. Twenty experiments were also conducted in the absence of oxygen over the same range of operating conditions to assess the role of the global water-gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, in CO consumption. Inlet molar feed ratios of oxygen to carbon monoxide were varied from 0.15 to 8.2--both above and below the stoichiometric value of 0.5. Residence times in the tubular reactor ranged from 5.0 to 12.1s, resulting in observed conversions ranging from 4.0 to 93%.

Like hydrogen, carbon monoxide oxidation in supercritical water was found to proceed after a pronounced induction period. The duration of the induction period for carbon monoxide oxidation was found to be the same or slightly shorter than that for hydrogen oxidation and was independent of the fuel equivalence ratio. Unlike hydrogen, the rate of carbon monoxide oxidation was found to be oxygen dependent, with a regressed global order of 0.34.

A considerable amount of hydrogen was formed over the course of low-temperature runs. Hydrogen formation was found to be strongly dependent on the fuel-equivalence ratio, with fuel-rich conditions favoring its formation. In addition, the rate of carbon monoxide consumption was found to be strongly pressure dependent, with higher pressures resulting in higher rates of consumption. The apparent, first-order rate constant was found to vary by a factor of 3 to 4 over the range of pressures studied. An in-depth discussion of the carbon monoxide oxidation data can be found in Holgate (1993) and in Holgate et al (1993), and Holgate and Tester (1994a,b).

2.2.2 Elementary reaction modeling

The elementary reaction model developed for carbon monoxide oxidation was somewhat less successful in describing the experimental oxidation data than was the hydrogen model. Good agreement between model predictions and data was obtained at high-temperatures under stoichiometric and fuel-rich conditions. The rate behavior and species concentration profiles for fuel-lean and low-temperature conditions, however, were not correctly predicted by the model. In addition, the model did not display the experimentally-observed oxygen dependence. It did, however, predict the formation of hydrogen--a feature lacking in previous CO modeling efforts. The duration of the observed induction periods are under predicted. The CO oxidation model also predicts the same induction time for all equivalence ratios, indicating the same independence of induction time on equivalence ratios as was seen in the hydrogen model and experiments.

The H_2/O_2 mechanism which successfully described SCWO of hydrogen was used as the starting point for the CO oxidation mechanism. Reactions involving carbon-containing species were then added to the validated H_2/O_2 SCWO submechanism. The complete carbon monoxide oxidation mechanism was comprised of 28 reversible reactions and 11 species (those present in the hydrogen mechanism plus CO, CO_2 , and HCO).

Analysis of the mechanism reveals that the oxidation of carbon monoxide occurs primarily via the reaction $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$. In most other respects, the essential features of the mechanism are similar to those of the hydrogen mechanism but with CO as the fuel. The pressure dependence of the oxidation rate is fairly well captured in the model and, as in the hydrogen mechanism, can be largely attributed to the effect of changing water concentration on rate of the branching reaction: $\text{H}_2\text{O} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{OH}$. The magnitude of the predicted pressure dependence is not as large as that observed, with the model predictions becoming increasingly poor at elevated pressures. A detailed discussion of the model and its comparison to data can be found in Holgate (1993) and in Holgate and Tester, (1994b).

3.0 LIST OF PUBLICATIONS AND THESES

Holgate, H.R. "Oxidation chemistry and kinetics in supercritical water: hydrogen, carbon monoxide, and glucose." Doctoral thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA (1993).

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4.0 LIST OF PARTICIPATING PERSONNEL

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5.0 REPORT OF INVENTIONS

Not applicable

6.0 BIBLIOGRAPHY

See Section 3

7.0 APPENDIXES

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